Suplimentary materials for "Commercial gold nanoparticles on untreated aluminum foil: versatile, sensitive and cost-effective SERS substrate "

by Kristina Gudun, Zarina Elemesova, Laura Khamkhash, Ekaterina Ralchenko and Rostislav. Bukasov

AuNPs@untreated Al foil substrate fabrication

Initially, normal microscopic glass slides were cut to about 1.2 cm x 1.2cm size and rinsed with Millipore water. Then glass slides were dried in the air and Al foil was attached Al foil to the glass with a double-sided scotch tape. We prepared analyte solutions of different concentrations. NBT and CV were dissolved in acetonitrile, paracetomol and KNO_3 in DI water. Standard solutions were obtained by serial dilutions of more concentrated solutions. Before applying prepared solutions we used parafilm to limit spreading of the drop on aluminum surface. We rinsed the addresses with DI water and applied 25 µl of prepared AuNP solution. 1 mL of commersial gold nanoparticles (Sigma, OD = 1) had been centrifuged and after removal of supernatant, resuspended in DI water several times (usually 2 or 3) and sonicated before and after all those cycles. Finally it was resuspended in lower volume of DI water 0.35-0.45 mL to prepare more concentrated solution of nanoparticles (OD about 1.5-2). Centrifugation parameters varied depending on nanoparticle *40 nm* – 5000 g for 12 min, *60 nm* – 2500 gfor 10 min. Finally, after suspension of AuNPs dried on the surface of Al foil, we applied 25 µl of analyte solution for each prepared address and meassured its Raman signal after analyte solution dried.

Fig1.AuNP solution dropped onto AuNP@Al foil.

Raman spectra (solid and SERS) of analyzed chemicals

The Raman measurements were performed with 785 nm diode and 633 nm He-Ne lasers (LABRAM Horiba) as described in the text of the paper. Background corrected spectral intensities obtained from 4 or16 maps (only for NBT and CV) were taken in different locations, but within 0.5-1.5 mm from the center of each address. They were averaged (64+ spectra in each map) for each sample. Representative Raman spectra for each analysed chemical are shown on figures below.

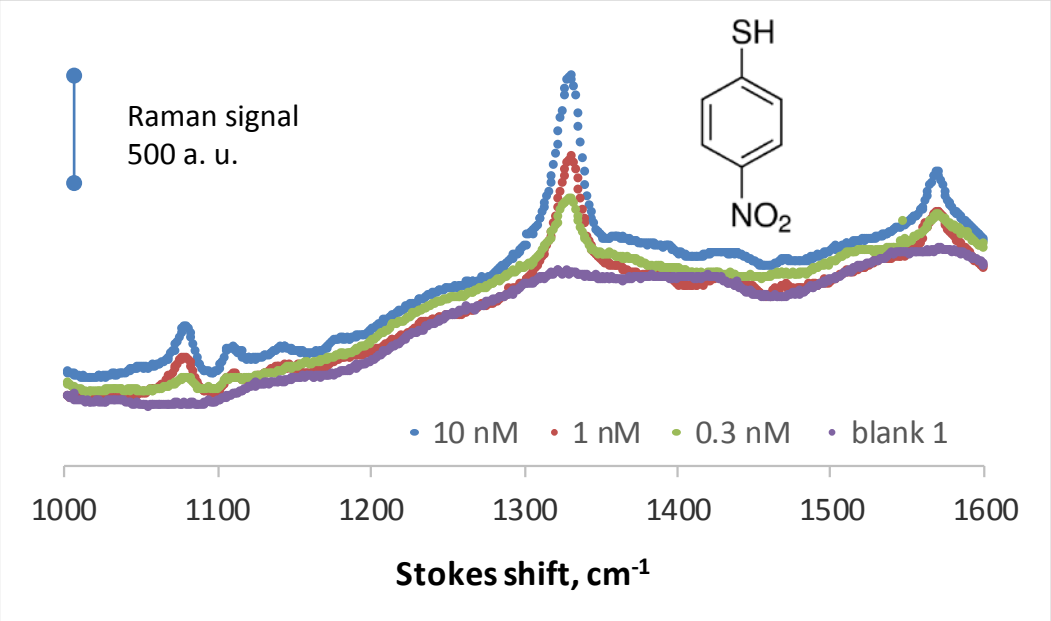

Figure 2. SERS spectra of NBT on 60 nm AuNPs @ Al foil at various concentrations of NBT, taken with 633 nm excitation wavelength.

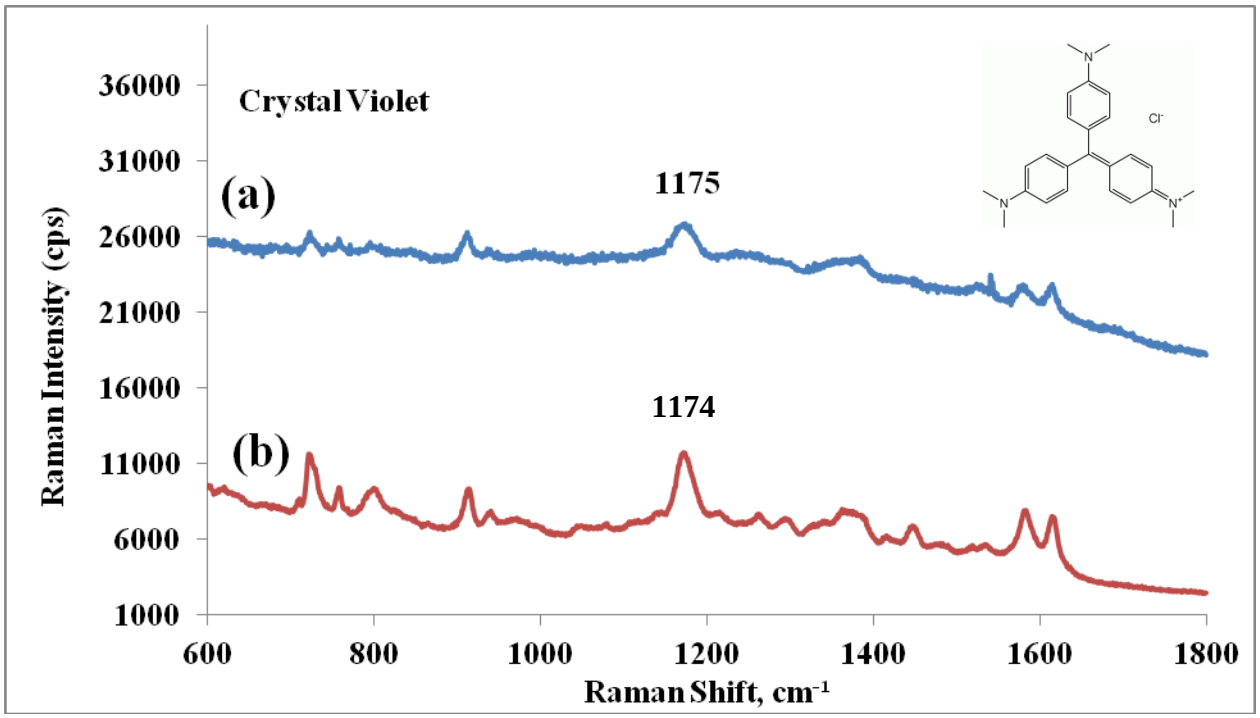

Fig. 3. Raman spectrum of solid CV(a) and SERS spectrum of 10^{-5}mol/L CV dropcasted onto 60 nm AuNP@Al foil (b), taken with 633 nm excitation wavelength .

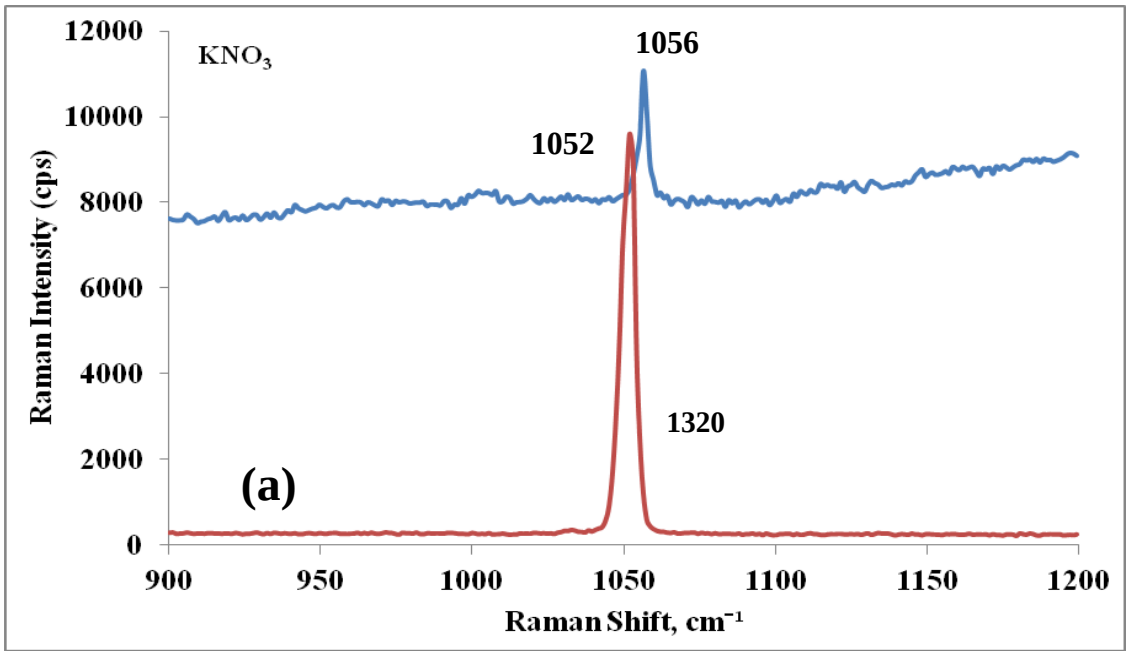

Fig. 4. Raman spectrum of solid KNO_3 powder (a) and SERS spectrum of $16x10^{-3}$ mol/L KNO_3 dropped onto 40 nm AuNP@Al foil (b), taken with 785 nm excitation wavelength.

AFM Characterization of AuNP@Alfoil substrate

The AFM measurements were done in tapping mode to obtain at least 3-7 AFM maps (10 x 10, 7 x 7 and 4 x 4 µm) with total of 700+ AuNPs for each representative sample. The average surface concentration and average fraction of agglomerated particles were calculated from counting all those AuNPs. The examples of AFM raw data are shown below.

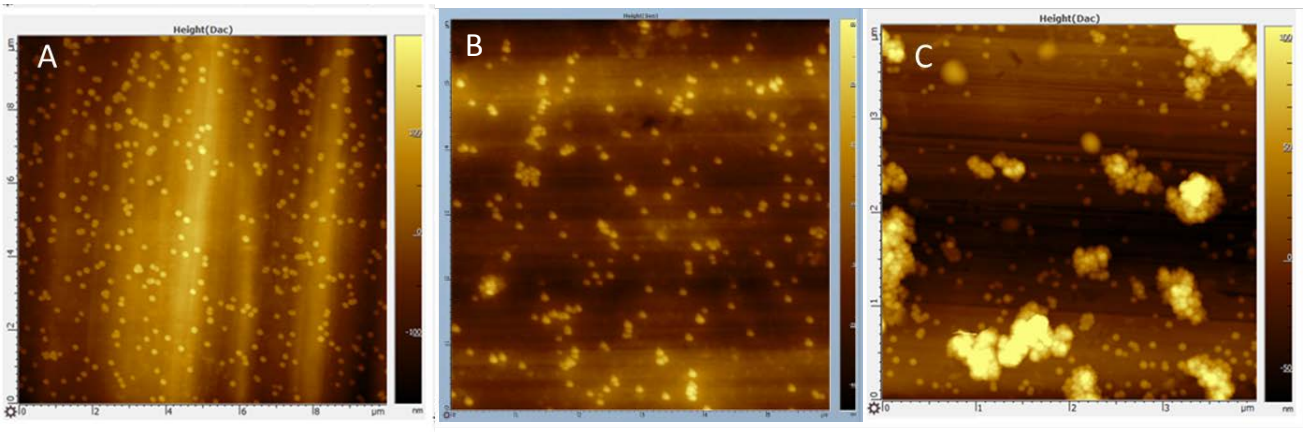

Fig.5. Unprocessed AFM images of AuNP@Al foil substrate: A) 60 nm AuNPs for CV, B) 60 nm AuNPs for NBT, C) 40 nm AuNPs for KNO_3.

Enhancement Factor Calculation

SERS enhancement factor, **EF**is given by,

$$EF = \frac{(I_{SERS}/N_{SERS})}{(I_{RAMAN}/N_{BULK})} = \frac{I_{SERS} N v_{BULK} z_{laser}}{I_{RAMAN} C_s} \quad (1)$$

where, $I_{SERS}$is the intensity of the particular peak of analyte when measured on SERS substrates (enhanced signal) whileI_{RAMAN}represents the intensity of same peak in un-enhanced Raman spectra measured in solid form. N_{SERS} is the number of analyte molecule contributing to the SERS signal on the substrate excited by laser beam and N_{BULK} is the number of molecules contributing to the un-enhanced Raman signal.[1]By incorporating the number of molecules in µm^3 ($N v_{BULK}$), average height of focused laser beam in µm (z_{laser}) and SERS surface concentration, number of molecules per µm^2 (C_s) EF can be rewritten as the second part of equation (1).

Example of EF calculation for NBT which is reported in first row in the table below:

$AEF_{(NBT)} = (177/230)/(14531/2.3 \times 10^{11}) = 1.2 \times 10^7$

This equation was used to calculate the EF for all other analytes. The calculation of each EF reported in the Table One on the next page

Table 1. Calculation of EFs for SERS on AuNP@Al andAuNPs@Au Film (marked*) substrates.

Analyte	AuNP D, nm; # of CF		Confocal depth, μm;λ laser, nm	Density, g/cm3; Molecular weight, g/mol	I SERS (blank adjusted normalized intensity)	I raman, intensity of solid bulk analyte	N_{SERS}	N_{BULK}	AEF
NBT	60; 3	3.00E-10	44; 633	1.36; 155	177	14531	230	2.30E+11	1.2E+07
NBT	60; 1	3.20E-09	44; 633	1.36; 155	13	14531	2451	2.30E+11	8.4E+04
NBT	bare Al foil	2.50E-04	69; 785	1.36; 155	1244	14531	1.30E+08	3.60E+11	237
CV	bare Al foil	1.00E-03	44; 633	1.19; 408	131	3708	3.30E+07	7.70E+10	82
CV	60; 3	3.00E-10	44; 633	1.19; 408	61	3708	230	7.7E+10	5.5E+06
KNO_3	40; 2	5.00E-05	69; 785	2.11; 101	182	2072	3.83E+07	8.70E+11	1995
Melamine	60, 3	6.20E-07	69;785	1.57; 126	74	5200	4.75E+05	5.20E+11	1.6E+04
NBT *LB*	60; 3	3E-10	44; 633	1.36; 155	177	112	230	2.65E+09	8.3E+06
CV *LB*	60; 3	3E-10	44; 633	1.19; 408	61	107	230	2.65E+09	6.6E+06
Melamine* LB*	60, 3	6.20E-07	69;785	1.57; 126	74	19	4.75E+05	4.15E+09	3.4E+04

CF is number of centrifugation/resuspension cycles. AEF is analytical enhancement factor

For all EF calculated we used bulk Raman signal measured for solid analytes, except three last rows, e. g. NBT *LB* and CV *LB* etc., where EFs are calculated using bulk Raman signal from 0.1 M solutions of CV, NBT and melamine. Both ways to calculate AEF produce results of similar magnitude within factor of about x2 difference between them.

Limit of Detection (LOD) Calculation

We calculated the LOD as a concentration of analyte at three standard deviations of the blank from the plot of blank adjusted signal vs analyte concentration.

$$\text{LOD} = 10^{\left(\log LOD = \frac{3std - b}{a}\right)} \quad (2)$$

where ***3std*** is the 3 standard deviation of the blank and ***a*** and ***b*** are the slope and the intercept of the linear calibration plot respectively.

Confocal length calculation for enhancement factor

A necessary factor for the calculation of enhanced factors is a confocal depth. In principle, all molecules within the illuminated volume of the solution can generate a Raman signal. The molecules in the focal plane contribute the most to the overall intensity and the contribution decreases dramatically from the molecules in the plane with increasing distance (z) to the ideal focal plane (z=0). The *h* value (in micrometers) depends on laser beam, the pinhole size and the objective lens of the Raman microscope. In order to estimate the number of molecules contributing to the total signal of the solid, we measured Raman signal of solid 4-NBT with different laser beam (*785 nm* and *633nm*) and objective (*50x*), which were used in surface Raman measurement. We took width of the bell curve (signal vs z distance from the focal plane) curve at 40% of maximum Raman intensity at focal plane as a confocal depth, micrometers, following figures illustrating confocal depth calculation in reference [1] and [2]. In fact if we calculated confocal depth as the ratio of normalized intensity integrated over confocal depth to the maximum normalized intensity, it would be at least as high as the curve width at 40 % intensity for each laser-objective configuration.

$$h = \frac{\int_{-\infty}^{\infty} I(z)dz}{I_{max}} \quad (3)$$

For instance, the sum of normalized intensity in the range from -100 to +100 microns divided by maximum normalized intensity is equal to 69 µm, as shown in the figure bellow. The confocal length is rather underestimated, because we cannot sup up intensity from -∞ up to +∞, but sum up the intensity only in the limited range. Therefore, the enhancement factors are very conservatively estimated.

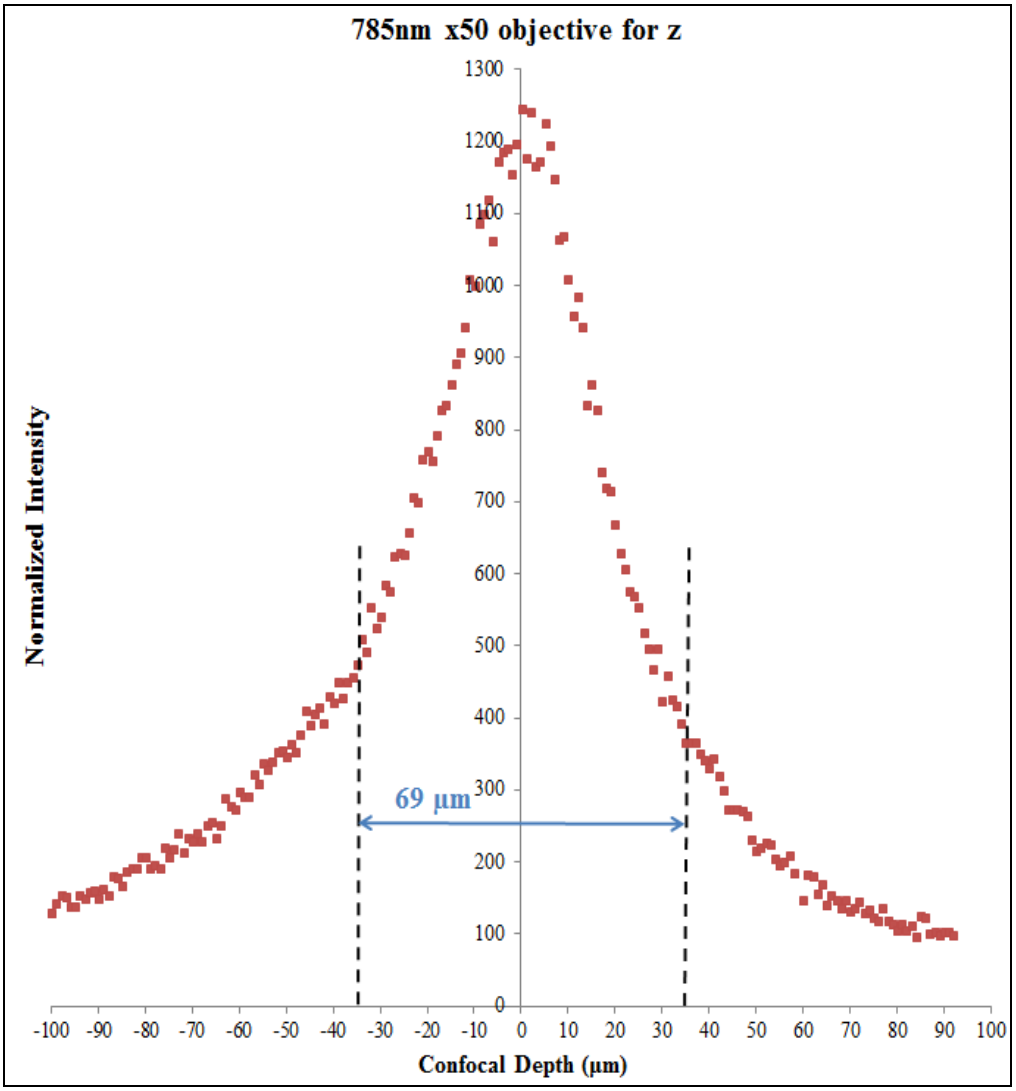

Fig. 6.Raman intensity(I) –confocal depth (z) profile of the normalized intensity of solid 4-NBT.SERS measurements are performed using *785 nm* excitation from a He-Ne laser and a *50X* long working-length objective.[2]

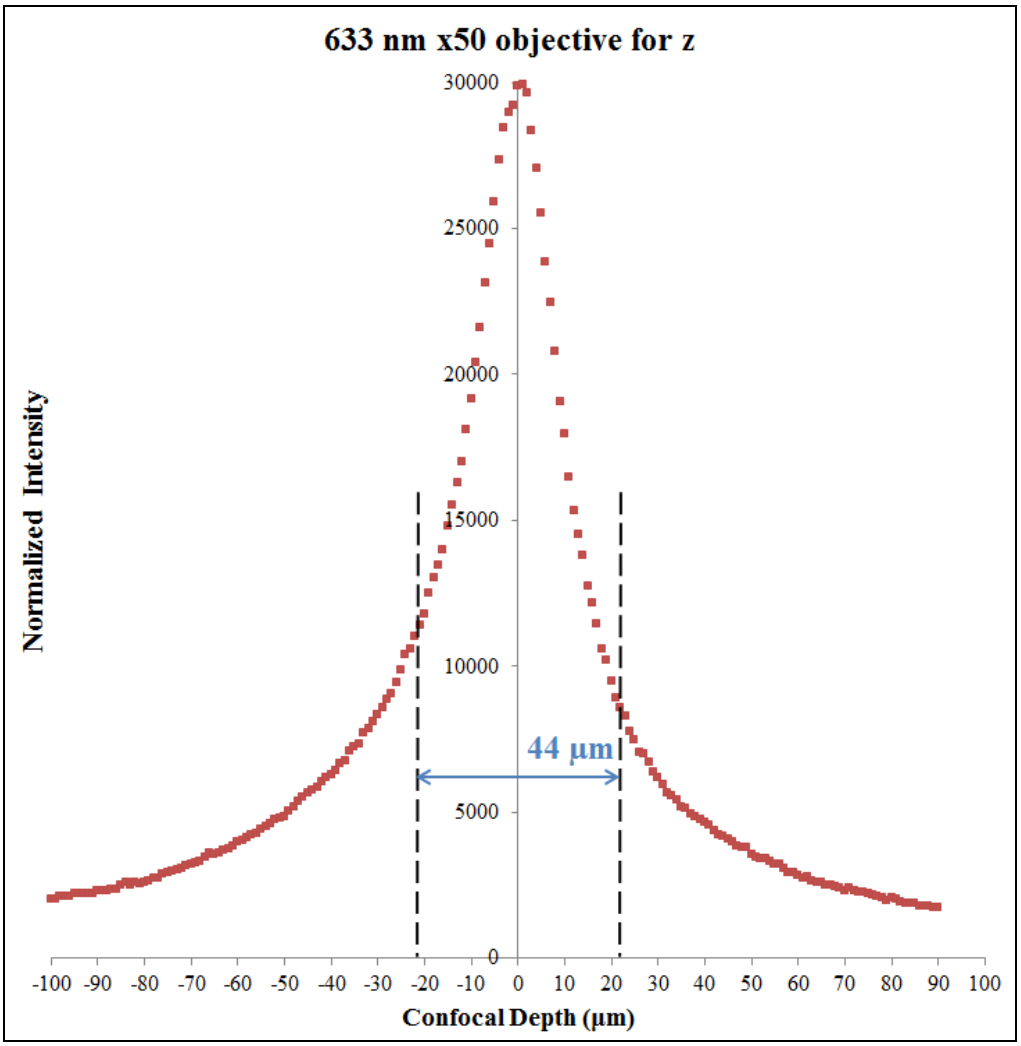

Fig. 7.Raman intensity(I) –confocal depth (z) profile of the normalized intensity of solid 4-NBT.SERS measurement were performed using *633 nm* excitation from a He-Ne laser and a *50X* objective

References

1. **X. M. Lin, Y. Cui, Y. H. Xu, B. Ren and Z. Q. Tian, *Anal Bioanal Chem*, 2009, 394, 1729-1745.**

2. **B. Ren, G. K. Liu, X. B. Lian, Z. L. Yang and Z. Q. Tian, *Anal Bioanal Chem*, 2007, 388, 29-45.**